

# **MEASUREMENT OF VISCOSITY OF HIGH ALUMINA BLAST FURNACE SLAGS BY STATISTICAL APPROACH**

**THIS THESIS IS SUBMITTED IN THE PARTIAL  
FULLFILLMENT OF THE REQUIREMNT FOR THE DEGREE OF  
BACHELOR OF TECHNOLOGY  
IN  
METALLURGICAL AND MATERIALS ENGINEERING  
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2015**



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## CERTIFICATE

This is to certify that the thesis entitled **“MEASUREMENT OF VISCOSITY OF HIGH ALUMINA BLAST FURNACE SLAGS BY STATISTICAL APPROACH”** submitted by Deepak Khandelwal (111MM0517) and Vinod Sanapala (111MM0458) in partial fulfillment of the requirements for the award of BACHELOR OF TECHNOLOGY Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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## **ACKNOWLEDGEMENT**

We avail this opportunity to express our indebtedness to our guide Prof. Smarajit Sarkar, Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela, for his valuable guidance, constant encouragement and kind help at various stages for the execution of this dissertation work.

We are grateful to Mr. Trinath Talapaneni, Department of Metallurgical and Materials Engineering, for providing valuable assistance and insight during the whole process.

We also express our sincere gratitude to Prof. Subash Chandra Mishra, Head of the Department, Metallurgical and Materials Engineering for allowing access to valuable facilities in the department.

And last but not the least; we thank all those friends who helped us in the course of this entire dissertation work.

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## **ABSTRACT**

Slag viscosity is an important process variable of the blast furnace process. The viscosity of molten slag is dependent basically on its chemical composition and on its temperature. Indian blast furnaces run into high alumina slag ( $\text{Al}_2\text{O}_3 \geq 25\%$ ) due to high alumina/silica ratio in iron ore as well as sinter and high ash content in the coke. These slags are highly viscous which affects the gas permeability, heat transfer etc. In the present work slag viscosity was determined for  $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$  quaternary system using Iida model. Slag composition consists of MgO values between 4 and 10%,  $\text{CaO/SiO}_2$  between 0.9 to 1.2 and  $\text{Al}_2\text{O}_3$  25%. The temperature range was between 1523 and 1723K which covers the liquidus temperature because the viscosity at this temperature will fluctuate greatly. The effect of  $\text{CaO/SiO}_2$ , MgO and temperature on viscosity were studied. The results indicate that the viscosity decreases with increase in basicity and MgO content.

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# **1. INTRODUCTION**



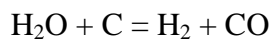
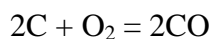
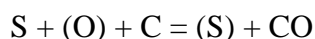
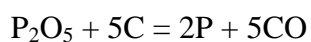
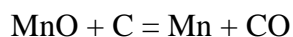
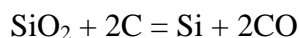
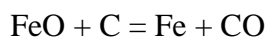
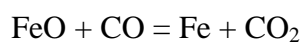
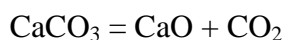
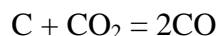
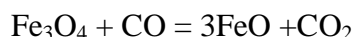
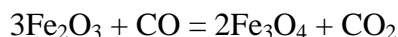
## **1.1 BLAST FURNACE:**

The blast furnace is a huge steel stack, lined with refractory brick, where dumping of iron ore, coke and limestone are done from the top, and from the bottom, the preheated air is sent in. About 6 to 8 hours is taken by the raw materials to descend to the hearth region of the furnace and the final products are liquid iron and liquid slag. The tapping of these liquid products is done at regular intervals. The bottom blown hot air takes about 6 to 8 seconds from the tuyeres region to the top of the furnace after going through numerous chemical reactions. The blast furnace has thick sides made of steel and lined with refractory bricks, to ensure no heat loss.

While the mixture of iron ore, coke and limestone heats, at the same time the hot waste gases are collected and cleansed. They are then used to help heat the air blast, required if blast furnace is to reach the high temperatures needed to produce molten iron.

The stock level is constantly 'topped up'. Molten iron ore is 'tapped' at the bottom of the blast furnace, poured into the iron ladle and removed for use. The purpose of a blast furnace is to physically convert and chemically reduce iron oxides into liquid iron called "hot metal".

The reactions that take place in a Blast furnace are as follows:



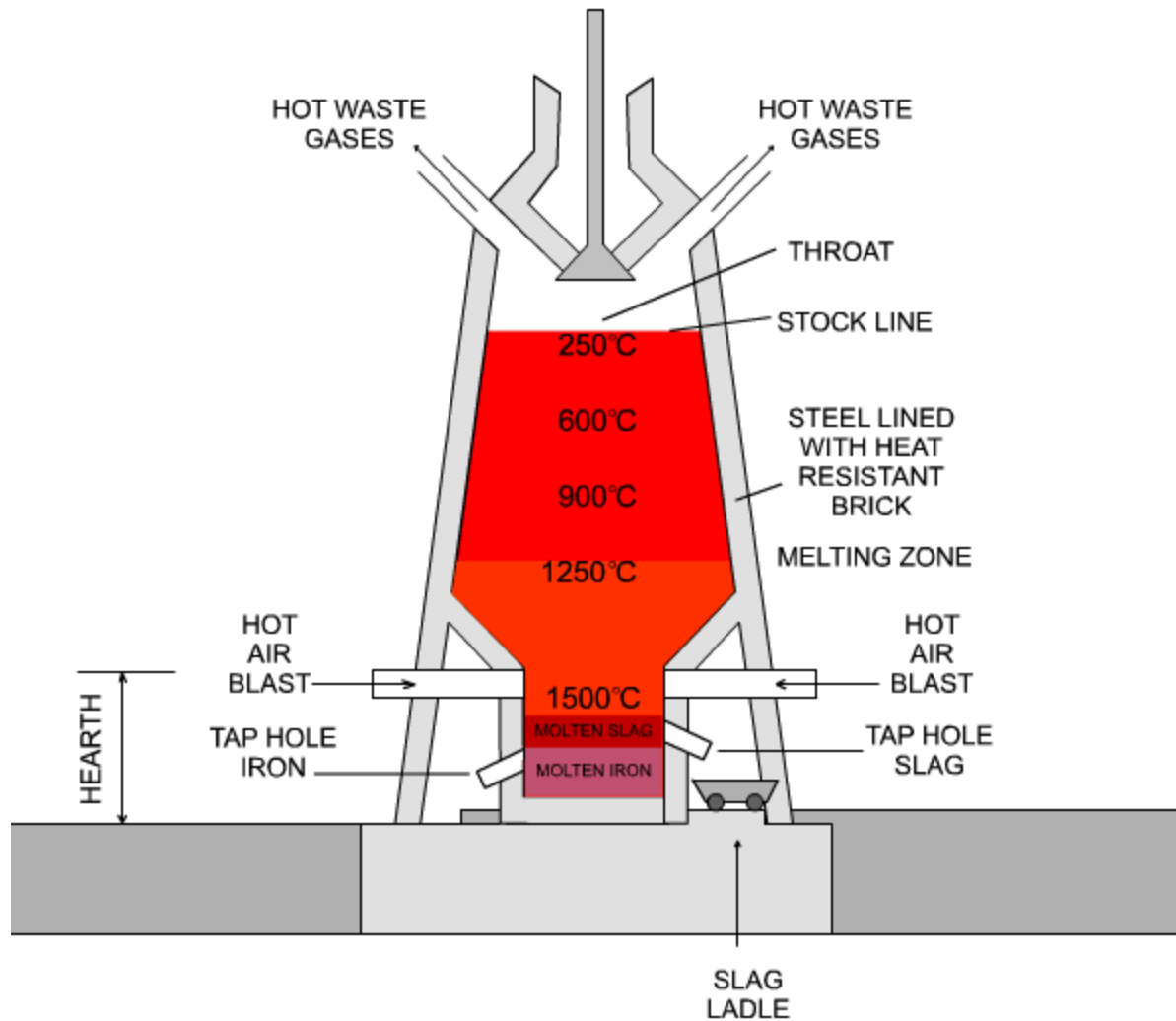


Fig.1: Overview of a Blast furnace.

## **1.2 BLAST FURNACE SLAG:**

The production of hot metal, the thermo-chemical reduction in a blast furnace leads to the formation of blast furnace slags. During this process which occurs continuously, iron ore or pellets as well as fluxes (limestone and/or dolomite) in the presence of heated air are heated under reducing conditions. Coke and other reducing agents (e.g. injected coal) are combusted to produce carbon monoxide which in turn reduces the iron ore or pellets to liquid hot metal.

The fluxes, the residues from the carbon source and the non-metallic components of the iron ore are chemically combined and result in the non-metallic liquid blast furnace slag. Hot metal and liquid slag accumulate at the bottom of the blast furnace, where the less dense slag forms a layer above the molten iron and can be separated in the skimmer. The

temperature of the blast furnace slag at tapping is around 1500 °C. BF slag can be cooled in several ways to form any of several types of BF slag products.

### **1.3 SLAG FORMATION & COMPOSITION:**

Minerals such as silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) are present in commercial ores. These are collectively referred to as the gangue and they are the basis of the slag that collects in the hearth of the furnace. Ash resulting from the combustion of coke also finds its way into the slag. The formation of a fusible slag is encouraged by the inclusion of fluxes in the burden and materials containing lime ( $\text{CaO}$ ) and magnesia ( $\text{MgO}$ ) are used to produce a slag with the desired composition.

The major constituents of blast furnace slags are the four oxides  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and the sum of their concentrations usually exceeds 95%. Compositions typically lie in the following ranges with only minor amounts of other oxides:

Table 1: Components and percentage of blast furnace slags.

Constituent	Percentage (%)
$\text{CaO}$	38 – 44
$\text{MgO}$	08 – 10
$\text{SiO}_2$	34 – 38
$\text{Al}_2\text{O}_3$	10 – 12
$\text{MnO}$	0.5 – 1.0
S	01 – 02
$\text{K}_2\text{O}$	0.1 – 0.6
$\text{FeO}$	< 0.2

Melting temperatures vary between 1200 °C and 1400 °C. In general, the chemical character of an oxide slag is determined by its composition and the various constituents are classified as either acid or basic, e.g.

Acidic oxides:  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  etc.

Basic oxides:  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{FeO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  etc.

Intermediate oxides:  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  etc.

## **1.4 SLAG VISCOSITY:**

Viscosity is a measure of the internal friction of a fluid. This friction becomes apparent when a layer of a fluid is made to move in relation to another layer. The greater the friction, the greater amount of force required to cause this movement. [1]

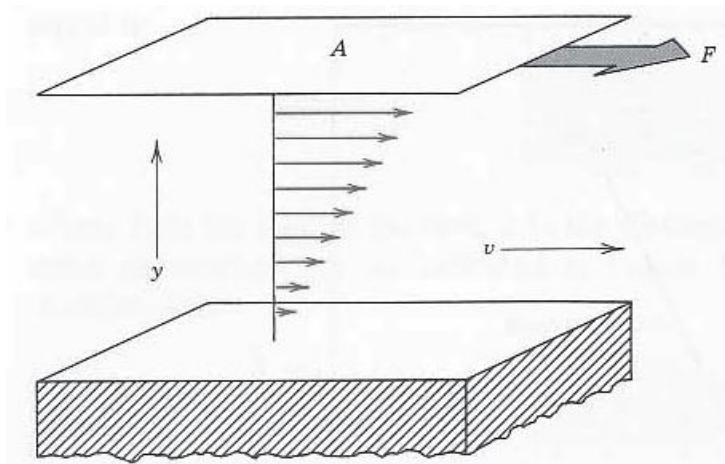


Fig.2: Representation of the viscous flow of a liquid when a shear force is applied.

$$\text{viscosity} = \frac{\text{shear stress}}{\text{shear rate}} = \frac{F}{A} \div \frac{\Delta v}{\Delta y}$$

The term  $F/A$  indicates the force per unit area required to produce shearing action “shear stress” and  $dv/dy$  is a measure of the change of speed at which the intermediate layers move with respect to each other and is called “shear rate”. Most metallic melts and molten slags are Newtonian fluids where the viscosities are independent of the shear rate, and thus the viscosity is defined according to Newton’s law as the proportionality constant between the shear stress and the velocity gradient normal to the shear stress (Figure 2). [2][3]

Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity. Both Newtonian and non-Newtonian behavior has been observed in slag systems. Non-Newtonian behavior is complex and can involve pseudo plastic flow of the fluids. Newtonian behavior has been reported to occur in slag systems containing less than 10–40 vol. % solids.

Viscosity controls the fluidity of slag. The slag should be fluid so that it can be removed easily during tapping of steel. In fact fluidity is inversely proportional to viscosity of slag. Molten slags are made up of discrete ionic structural units and their activation

energy is closely related to the type of ions and ionic complexes present as well as the interionic forces they give rise to. In general viscosity of a slag is a function of temperature, composition and percent solid present in slag, or a given temperature.

Since increased temperature loosens up the structure, the viscosity will decrease with increasing temperature. Usually viscosity is exponentially proportional to inverse temperature; however at a certain temperature, very small changes in temperature can result in large changes in viscosity. This temperature is called a temperature of critical viscosity. The nature of such phenomenon is related to the crystallization of the solid phase from the melt, which in turn, affects the slag viscosity behavior. [4]

The temperature dependence of the viscosity is usually expressed in the forms of the Arrhenius relationship [5]:

$$\mu(T) = \mu_0 \exp\left(\frac{E}{RT}\right)$$

Where T is temperature,  $\mu_0$  is a coefficient, E is the activation energy and R is the universal gas constant.

### **1.5: OBJECTIVE:**

The iron ores usually found in India has the alumina content of about 2% and higher. Such ores raise the alumina levels in the blast furnace slags to about 20% or more. Slags with higher  $\text{Al}_2\text{O}_3$  content have higher viscosity thus reducing the slag drainage rate. Such slags are difficult to operate since with the increase in the  $\text{Al}_2\text{O}_3$  content of the slag, the blast furnace operations has difficulties such as accumulation of molten slag in the blast furnace hearth and increase in the pressure drop at the lower part of the furnace.

Higher alumina slag has greater tendency towards silicon reduction and there is tendency towards increase of hot metal silicon level. The sulphur content of the hot metal tends to increase with the increase in the alumina content of the slag. Hence the high alumina slags contributes to less efficient desulphurization.

Hence it is important to keep good slag fluidity in the blast furnace operation for keeping good permeability and good drainage of slag during tapping. So even with the presence of the high  $\text{Al}_2\text{O}_3$  slags it is important to have a good fluidity slag in the blast furnace. In this particular project we find out the best combination of high alumina blast furnace slags in terms of MgO and C/S ratio for a better fluidity. For that we use the statistical approach to find the variation of viscosity of the slags with change in MgO content and the change in basicity.

## **2. LITERATURE SURVEY**

**2.1 Y.S.LEE, J.R.KIM, S.H.YI and D.J.MIN [6]** made their studies to find the viscosity variations of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$  slag system under varying concentrations of the contents. They used blast furnace slags for this purpose. And they performed experiments to derive their conclusion. They varied their basicity from 1.15 to 1.6, composition of  $\text{Al}_2\text{O}_3$  from 10 to 13 mass percent, composition of  $\text{MgO}$  from 5 to 10 mass percent and the composition of  $\text{FeO}$  from 5 to 20 percent. Apart from the experiments they also carried out a thermodynamic approach to attain a relationship between viscosity and slag components using the experimental results.

They found out that at a basicity of 1.5 the viscosity of slags will increase from 2.5 dPas to about 10 dPas when the  $\text{FeO}$  content is decreased from 10 to 5 mass percent. They also found that at fixed composition of  $\text{MgO}$  and  $\text{FeO}$  the viscosity of the slags increases when the basicity is increased from 1.4 to 1.6. They even concluded that the general bosh slags which contain  $\text{FeO}$  of less than 7.5 percent show high viscosity. They cited the reason is that the effect of basicity and  $\text{MgO}$  can be of great dominance on the slag viscosity. So, because of this, the reduction rate of  $\text{FeO}$  may affect the fluidity of slag in the bosh level of the blast furnace. A proposal has been made that even though at a constant temperature the behavior of slag is that of a homogeneous liquid, the slag viscosity is also affected by the melting point of slag and not only by the depolymerization mechanisms of silicate network.

Their studies even concluded that there is a decrease in the viscosity of the blast furnace slags when the  $\text{FeO}$  content is increased at a fixed basicity. A minimum value of slag viscosity is attained by them when the  $\text{MgO}$  composition of the slag is increased at a low content of  $\text{FeO}$  of about less than 7.5 mass percent. At  $\text{FeO}$  composition greater than 7.5 mass percent the increase in the  $\text{MgO}$  content of the slag does not affect the viscosity of slag. The authors found the minimum viscosity values at  $\text{MgO}$  composition of 7 mass percent and  $\text{FeO}$  composition of 5 mass percent. Their studies also indicated that with the increase in the slag basicity, the viscosity decreased until basicity of 1.3 and on further increase upto 1.5 the viscosity increased. Hence a proposal had been made that when the basicity is increased to less than 1.3, the depolymerization of silicate network act as the driving force for the decrease in viscosity while at basicity values of greater than 1.3, the increase in the chemical potential of solid compounds is the driving force which results in the increase of the viscosity of slag. In their studies a reasonable relationship is obtained between the slag components and the viscous behavior of the basic blast furnace slags (or bosh slags) with the help of the thermodynamic approach for the activity of primary solid phase.

**2.2 YUN-MING GAO, SHAO-BO WANG, CHUAN HONG, XIN-JUAN MA and FU YANG [7]** investigated the effect of varying basicity and varying  $\text{MgO}$  content on  $\text{SiO}_2\text{-CaO-MgO-9\%Al}_2\text{O}_3$  slag system. For this experiment they used the rotating cylinder method. They varied the basicity from 0.4 to 1.0 and also the  $\text{MgO}$  content from 13 to 19 weight percent. The

temperature range of 1573K to 1813K is maintained. They verified the slag structure and viscosity correlation using the Fourier transform infrared (FTIR) spectroscopy. They examined the slag's phase characteristics by the X-ray diffraction method (XRD). Thermodynamic software named Factsage is used to calculate the liquidus temperature of each slag. Their results can be summarized as below:

- With the increase in the MgO composition of the slag or increase in the basicity of the slag, there is depolymerization of the slag melt's complex network structures into smaller and simpler network units for viscous flow. This is depicted by the FTIR analysis. Also among the two, in order to decrease the slag viscosity in an effective way, increasing the basicity of the slag is better when compared to increasing the MgO composition of the slag.
- The synergistic action of the basic oxide components of the slag strongly influences the viscosity of the slag. The degree of viscosity decrease on increasing the basicity/ MgO content, is higher at lower CaO and MgO contents when compared to higher CaO and MgO contents. At lower MgO content the basicity's effect on viscosity of the slag is quite significant and on increasing the MgO content from 13 to 19 weight percent, it becomes less pronounced. Similarly, at a lower basicity the effect of MgO content on the slag's viscosity is also significant and even this becomes less pronounced when the basicity is made to increase from 0.4 to 1.0.
- In the complete liquid region, for every slag, with the increase in temperature there is a smooth decrease in the viscosity of the slag. At higher temperatures, there is no appreciable decrease in the slag's viscosity (due to increase in the MgO composition or basicity of the slag) when compared to that at lower temperatures. The calculated activation energy of the viscous flow ranges between 154 and 200 kJ mol<sup>-1</sup>. This decreases if we increase the basicity from 0.4 to 1.0 at a constant MgO composition in the range of 13 to 19 weight percent.
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**2.3 LEI GAN and CHAOBIN LAI [8]** studied the viscosity characteristics for CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO slag system at various temperatures and by varying the basicity and MgO concentration. They have designed their own database which works on mass fraction ratios, liquidus temperatures to extrapolate the viscosity values. They used this model on varying concentrations of CaO (28 to 50 mass percent), SiO<sub>2</sub> (25 to 50 mass percent), Al<sub>2</sub>O<sub>3</sub> (5 to 36



mass percent) and MgO (2.5 to 25 mass percent). They also varied the weight fraction of CaO and SiO<sub>2</sub> from 0.7 to 1.5. Using that model they plotted iso-viscosity lines for the above mentioned blast furnace slags at 1623K, 1673K, 1723K and 1773K for 5mass%, 10mass% and 15mass% of MgO after making the required calculations. By the isoviscosity lines they concluded that within their selected range of blast furnace slags, there will be a decrease in the viscosity with the increase in the MgO composition and basicity. But they found that the viscosity increases when the Al<sub>2</sub>O<sub>3</sub> content increases. They also indicated that the variation of viscosity by variation of Al<sub>2</sub>O<sub>3</sub> content is similar to that of variation of SiO<sub>2</sub> content in the blast furnace slags.

**2.4 JIFANG XU, JIEYU ZHANG, CHANG JIE, GONGYUAN LIU and FEI RUAN [9]** studied the variation of the viscosity of selected quaternary CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags with variation of CaO/Al<sub>2</sub>O<sub>3</sub> ratio. The temperature at which the experiment is performed is about 1875K. The ratio of CaO/Al<sub>2</sub>O<sub>3</sub> is maintained between 0.97 and 2.19. The experiment is carried out using the rotating cylinder method. In this experiments they found out that on increasing the CaO/Al<sub>2</sub>O<sub>3</sub> ratio, the viscosity of the slag also increases to some extent. Beyond this, on further increase in the CaO/Al<sub>2</sub>O<sub>3</sub> ratio the viscosity of the slag decreases. They also indicated that in the statistical approach of high basicity and high Al<sub>2</sub>O<sub>3</sub> slags, the Iida model produce consistent results when compared to that of the experiment results.

**2.5 NORITAKA SAITO, NAOTO HORI, KUNHIKO NAKASHIMA and KATSUMI MORI [10]** studied the change in viscosity of 40CaO-40SiO<sub>2</sub>-20Al<sub>2</sub>O<sub>3</sub> (mass percent) due to addition of MgO, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> and the change in viscosity of CF (Mono calcium ferrite 26.1CaO-73.9Fe<sub>2</sub>O<sub>3</sub> (mass percent)) and that of CF<sub>2</sub> (Hemi- calcium ferrite 14.9CaO-85.1Fe<sub>2</sub>O<sub>3</sub> (mass percent)) due to the addition of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO. The viscosity measurements of the experiment were calculated using the cylinder rotating viscometer.

In their experiments it is seen that as soon as the slags melted the value of viscosity is very high. With the increase in the holding time, the viscosity kept decreasing and it finally became constant on holding from 1.5 to 11 hours depending on the composition of the slag. The CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags show decrease in the viscosity with the increase in the MgO, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> content. For a constant composition of the additive oxide, there is a decrease in the viscosity in the order of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and MgO. On increasing the additive oxide content in any of the systems, there is a decrease in the apparent activation energy of the viscous flow. On increasing the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content of the calcium ferrite slags; there is an increase in the viscosity of the slags. Compared to others, for a same content of the oxide, Al<sub>2</sub>O<sub>3</sub> shows effective increase in the viscosity. In any of the systems, with increase in the additive oxide's content, there is a decrease in the apparent activation energy of viscous flow.

**2.6 AMITABH SHANKAR, MARTEN GORNERUP, A.K. LAHIRI and S.SEETHARAMAN [11]** aimed to experimentally determine the viscosity of CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> slags. These are considered as high alumina blast furnace slags. The Al<sub>2</sub>O<sub>3</sub> content in the prepared slag samples varies from 20 and 30 mass percent. MgO content is varied between 2 and 5 mass percent. The TiO<sub>2</sub> concentration is varied between 0 and 2 mass percent. The basicity for the experiment is ranged between 0.8 and 1.2. The investigation's temperature is maintained between 1650 and 1873K. The investigation is done on the variation of viscosity of the earlier said slag samples with the change in Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and MgO. The authors also aimed at creating a database for the viscosity of high alumina blast furnace slags in order to formulate a suitable viscosity model and to optimize the BF slags with a varied range of temperature and slag chemistry.

After the studies the authors concluded that with the increase in the basicity of the blast furnace slag from 0.46 to 0.8, there is a decrease in the viscosity of the slag. In case of high basicity slags (basicity of about 0.8) even the addition of a small amount of TiO<sub>2</sub> (of about 2 mass percent) can decrease the viscosity of the slag. In the range of 0.1 and 0.4 basicity, there is an increase in the viscosity of the slag with the increase in the silica activity. Below the liquidus temperature, this increase is steeper. With the increase in the activity of silica there is an increase in the activation energy of both the slag systems.

**2.7 HAOYAN SUN, JINGSONG WANG, XIANGJUAN DONG and QINGGUO XUE [12]** determined the viscosities of Al<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub>-TiO<sub>2</sub> slag system by experimental methods. The slags used are low basicity slags with higher titanium content. The variation of TiO<sub>2</sub> was between 23 and 33 mass percent. Al<sub>2</sub>O<sub>3</sub> is varied in between 3 and 9 weight percent. The basicity (CaO/SiO<sub>2</sub> ratio) of the slags is maintained between 0.3 and 0.7. The investigation is done in the temperature range of 1573K and 1773K which covers the liquidus temperature range. Investigation is done on the variation of the viscosity with the effect of basicity, temperature, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc. of the slag system mentioned above. The authors also aimed at creating a database for the viscosity of high titanium blast furnace slags with low basicity in order to formulate a suitable viscosity model and to optimize the titanium slags with a varied range of temperature and slag chemistry.

Based on the results obtained they concluded saying that, with the increase in the TiO<sub>2</sub> content and basicity of the slag, there is a decrease in the viscosity of the slag. Above the liquidus temperature, the viscosity increases with the increase in the alumina content. Using the second derivatives of the activation energies for viscous flow w.r.t temperature, the liquidus temperature of the slags was evaluated. With the increase in the TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> composition of the slag, there is an increase in the liquidus temperature of the slag. The liquidus temperature decreases when there is an increase in the basicity.

**2.8 MASASHI NAKAMOTO, TOSHIHIRO TANAKA, JOONHO LEE and TATEO USUI [13]** performed experiments to attain viscosity values of slag systems and compared their experimental results with that of a statistical model derived by them. For their experiment they used molten  $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$  system with high CaO and  $\text{Al}_2\text{O}_3$  concentration to search for a slag with low melting temperature and low viscosity. They performed the experiment using the rotating cylinder method for viscosity calculations. They have prepared 3 slag samples of different concentrations and calculated the viscosity at about 1673K which is a general temperature in the blast furnace. They found out that viscosity increases with decreasing temperature. They have concluded from their experiments that at 1673K a slag with concentrations of 35mass%  $\text{Al}_2\text{O}_3$ , 43.1% CaO, 7.5mass% MgO, 14.4mass%  $\text{SiO}_2$  has the required viscosity of below 0.6 Pa.s. The results from their designed model also revealed the similar results.

**2.9 MAO CHEN, DIANWEI ZHANG, MINGYIN KOU and BAOJUN ZHAO [14]** aimed to compare the blast furnace slag's viscosity to that of the synthetic slags in order to check how accurate the present viscosities models are. For the same, they conducted experiments and calculated the viscosity of blast furnace slags using different models. They maintained a basicity of 1.1. The composition of the slag being used is about 17.2 weight percent  $\text{Al}_2\text{O}_3$ , 3 to 8.9 weight percent. The temperature is varied from 1675K to 1850K. Using the results, the authors checked the reliability of the modified quasi-chemical viscosity model.

**2.10 JING GUO, SHUSEN CHENG and HONGBO ZHAO [15]** studied the viscosity values of  $\text{SiO-CaO-MgO-Al}_2\text{O}_3$  slag system by a new model created by them using the ionic concentration of the ions of the atoms. They studied slags of basicity in the range of 0.5 to 1.60 and in a temperature range of 1573K to 1773K. In their studies they established a relation between viscous activation energy and silicate slag composition in a structure-based consideration. In the model they formulated a series of ion concentration for the molten slag systems. They compared the viscosity values attained from their model with those of the previously performed experiments. They applied their model to many other binary and ternary systems and obtained results having better accuracy and precision when compared with the experimental viscosity values.

**2.11 XIAO-JUN HU, ZHONG-SHAN REN, GUO-HUA ZHANG, LI-JUN WANG and KUO-CHIH CHOU [16]** proposed a reasonable, simple method to estimate the viscosity of  $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2$ ,  $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2\text{-MgO}$  and  $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2\text{-TiO}_2$  blast furnace slags by considering the fact that corrected optical basicity reflects the structural influence on viscosity.

To incorporate the influence of the effect of charge balance of  $\text{Al}^{+3}$  ions on viscosity by using corrected optical basicity, the viscosity of the above mentioned blast furnace slag system is calculated using a new model. They also concluded that the presence of higher content of  $\text{TiO}_2$  decreases the viscosity of the slags. It is because Ti-O bonds are weaker compared to that of Al-O and Si-O. Hence the degree of polymerization declines when  $\text{TiO}_2$  is present.

**2.12 GUO-HUA ZHANG, KUO-CHIH CHOU, QING-GUO XUE and KENNETH C. MILLS [17]** developed a viscosity model that is structurally related for the viscosity estimation of slag systems containing MgO, CaO, FeO, MnO and  $\text{SiO}_2$  with the variation of both temperature and composition of the components. In this particular model, the non-linear composition dependence of the activation energy is expressed with the calculation of oxygen ions. The variation of the slag viscosity with the variation of the different slag components is determined. The order of viscosity decreasing ability of the metal oxide for given mole fraction is  $\text{FeO} > \text{MnO} > \text{CaO} > \text{MgO}$ . The authors also proposed that because of the opposing influences of interaction and hindrance the viscosity is affected and hence the cation size has a role to play. They also concluded that the percentage of ionic bonding in the metal – oxygen bond may also affect the viscosity of the slags.

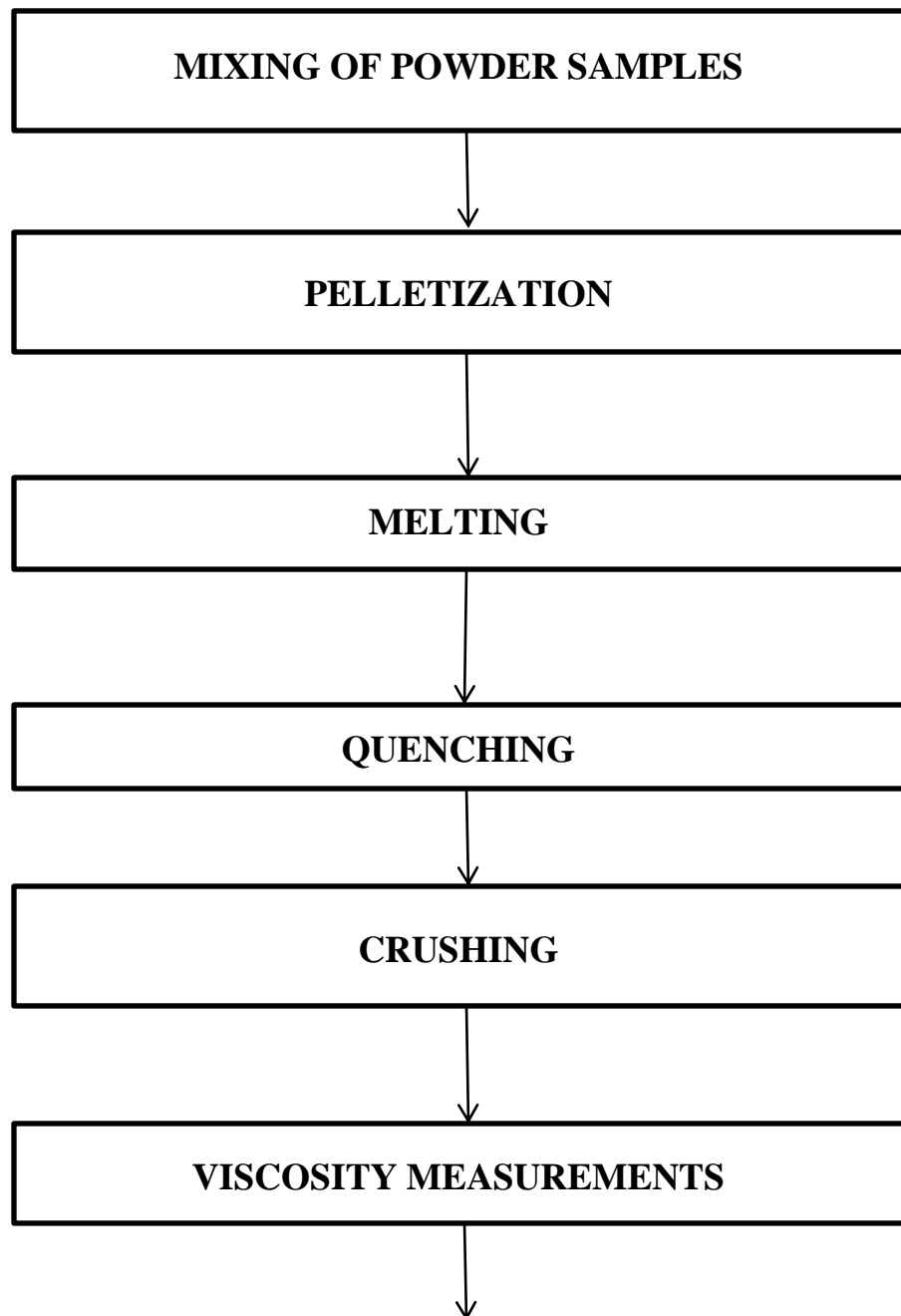
### **3. EXPERIMENTAL PROCEDURE**

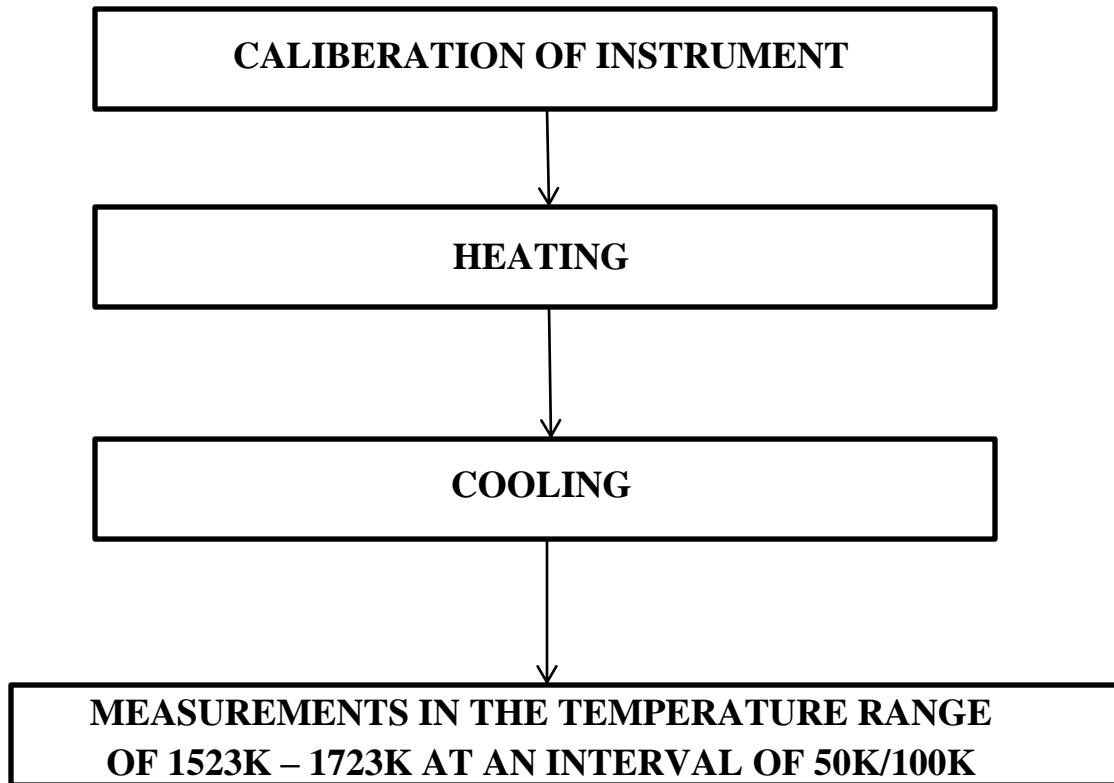
### **3.1 SLAG PREPARATION & VISCOSITY MEASUREMENT:**

- Pure oxides of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  are taken in required weights in a flask capable of holding 150 grams of this powder mixture.
- The slag composition determines the amount of oxides to be taken.
- Slag weighing 120 grams in total is prepared.
- For a slag having composition of 25%  $\text{Al}_2\text{O}_3$ ,  $\text{C/S}=1.15$  & 8%  $\text{MgO}$  then 30 grams of  $\text{Al}_2\text{O}_3$ , 43.005 grams of  $\text{CaO}$ , 37.395 grams of  $\text{SiO}_2$  & 9.6 grams of  $\text{MgO}$  is prepared. This powder is mixed in abrasion testing mixer for an hour.
- After mixing this we will convert this powder into pellets so that their accommodation in crucible is proper. Pelletisation is done by adding small amount of water & forming pellets of this powder. These pellets are dried in oven at a temperature of 120-150 °C.
- Now these pellets are placed in a rising hearth furnace at a temperature of 1773K for 30 mins in a platinum crucible.
- All of the pellets cannot be added at once as the crucible is small. Almost 50 to 60% is added at one go & the rest will be added after the melting of these pellets take place in furnace.
- These pellets are placed when the furnace is started. The furnace takes 3-4 hours to reach a temperature of 1773K. After reaching this temperature we need to hold the mixture in furnace for 30 mins.
- While the re-adding of remaining pellets is done, the furnace temperature will come down. Now after closing the furnace we need to wait until the furnace reaches its temperature & then we will hold it at that temperature for 30 mins.
- The melted mixture which is our desired slag is then quenched i.e. whole of the slag is put in water.
- The quenched slag is crushed into fine powder in a ball mill.
- Now slag is collected from water & placed for drying in an oven at 120-150°C so that all the moisture which was absorbed by it during quenching will be removed.
- Now platinum crucible is cleaned by boiling it in a dilute solution of  $\text{HCl}$  for 30 mins. If it isn't properly cleaned we need to again boil it for 15 mins.
- After this, slag may be sent for chemical analysis so that exact composition can be determined. This will give a precision in the experiment as this slag composition may change during the process. Chemical analysis is done by X-ray diffraction and the sample is sent for viscosity measurements.
- For the viscosity measurement, first a calibration measurement is carried out at room temperature by using a standard oil of known viscosity. This is done to ensure that our instrument is working properly & to apply necessary settings.
- The crucible of instrument is taken & prepared slag of 120gms is placed in the furnace.
- The furnace will heat at a rate of 10K/5K per minute upto 1873K.

- The furnace is kept for maximum temperature for atleast 1 hour to ensure proper melting of slag.
- Furnace is programmed to cool down at a rate of 2K per minute to a selected lower temperature which should be above slag's flow temperature.
- Viscosity data is measured at an interval of 50/100K. At these temperatures we need to keep furnace atleast for 30 mins for viscosity value.

### **3.2 FLOW CHART FOR VISCOSITY:**





### **3.3 MODEL FOR VISCOSITY MEASUREMENT:**

#### **3.3.1 The Iida Model:**

The relation between the basicity of the slag and structure is attained by the Iida model. Slags usually lie in any of the 3 types.

- a) Acid oxide ( $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , etc.)
- b) Basic oxide ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaF}_2$ , etc.)
- c) Amphoteric oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , etc.)

This model is based on the Arrhenius Equation by which the oxides are divided into two groups (a) and (b). The modified version has an additional group known as the third group, group (c).

The viscosity of slags can be attained by:

$$\mu = A \mu_o \exp \left( \frac{E}{B_i^*} \right) \quad \dots \quad (1)$$

Where, A and E are parameters, T= absolute temperature,  $\mu$  =viscosity,  $B_i^*$ = basicity index.



$$\begin{aligned} A &= 1.745 - 1.962 \times 10^{-3} T + 7.000 \times 10^{-7} T^2 & \dots & (2) \\ E &= 11.11 - 3.65 \times 10^{-3} T & \dots & (3) \end{aligned}$$

$\mu_{oi}$  values can be calculated by:

$$\mu_{oi} = 1.8 \times 10^{-7} \frac{[M_i(T_m)_i]^{1/2} \exp(H_i/RT)}{(V_m)_i^{2/3} \exp[H_i/R(T_m)_i]}$$

$$H_i = 5.1 (T_m)^{1.2}$$

Where  $T_i$  =mole fraction,  $T_m$  = melting temperature,  $\mu_o$ = hypothetical viscosity of pure oxide,  $R$ = universal gas constant,  $V_m$  =molar volume at melting point,  $M$  = the formula weight,  $i$ =component,  $B_i^*$  = modified basicity which can be calculated by the following equation:

$$B_i^* = \frac{\sum (\alpha_i W_i) B}{(\sum (\alpha_i W_i) + \alpha_{Al_2O_3}^* W_{Al_2O_3})}$$

Where  $\alpha$  = specific coefficient,  $A$  = acidic oxide,  $B$  = basic or fluoride oxide,  $W_i$  = mass percentage.

[Table 1] gives the value for  $\alpha_i$  and  $\mu_{oi}$  of different compositions.

$\alpha_i^*$ (modified specific coefficient) indicates the interaction between the amphoteric oxide and the other component that itself is dependent to  $B_i^*$  and  $W_i$ .

The value for  $\alpha_{Al_2O_3}^*$  can be calculated by Equation (6) which gives the best fit to experimental results.

$$\alpha_{Al_2O_3}^* = aB_i + bW_{Al_2O_3} + c \quad \dots (6)$$

Where,

$$a = 1.26 \times 10^{-5} T^2 - 4.3552 \times 10^{-2} T + 41.16$$

$$b = 1.40 \times 10^{-7} T^2 - 3.4449 \times 10^{-4} T + 0.2062$$

$$c = -8.00 \times 10^{-6} T^2 + 2.5568 \times 10^{-2} T - 22.16$$

If we consider  $\alpha_i^* = \alpha_i$ , then the modified basicity index ( $B_i^*$ ) will be the same as the basicity index ( $B_i$ ) [11].

### 3.3.2 Modified Iida model :

It is similar to the Iida model discussed above but only the value of A, E and B<sub>j</sub> are replaced by the following equations [11]:

$$A = 1.029 - 2.078 \times 10^{-3} T + 1.050 \times 10^{-6} T^2 \quad \dots \quad (7)$$

$$E = 28.46 - 2.0884 \times 10^{-2} T + 4.000 \times 10^{-6} T^2 \quad \dots \quad (8)$$

$$B_i^* = \frac{(\sum (\alpha_i W_i)_B + \sum (\alpha_i^* W_i)_{Am2})}{(\sum (\alpha_i W_i)_A + \sum (\alpha_i^* W_i)_{Am1})} \quad \dots \quad (9)$$

The amphoteric oxide may act as the basic oxide or the acid oxide which is dependent on the overall basicity of slag. In quaternary slag system of (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO) the modified basicity index (B<sub>j</sub>) and specific coefficient of (Al<sub>2</sub>O<sub>3</sub>) can be estimated by Equation (10-12)

$$B_i^{(j)} = \frac{(\alpha_{CaO} W_{CaO} + \alpha_{MgO} W_{MgO})}{(\alpha_{SiO_2} W_{SiO_2} + \alpha_{Al_2O_3}^* W_{Al_2O_3})} \quad \dots \quad (10)$$

$$\alpha_{Al_2O_3}^* = a B_i + b W_{Al_2O_3} + c \quad \dots \quad (11)$$

The value of  $\alpha_{Al_2O_3}^*$  can be positive or negative, means that Al<sub>2</sub>O<sub>3</sub> play a role as acidic oxide and basic oxide respectively.

$$\begin{aligned} \text{Where, } a &= 1.20 \times 10^{-5} T^2 - 4.3552 \times 10^{-2} T + 41.16 \\ b &= 1.40 \times 10^{-7} T^2 - 3.4944 \times 10^{-4} T + 0.2062 \\ c &= -8.00 \times 10^{-6} T^2 + 2.5568 \times 10^{-2} T - 22.16 \end{aligned}$$

## **4. RESULTS & DISCUSSION**

Viscosity measurements for the selected quaternary  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{MgO}$ - $\text{CaO}$  slag system were done. A total of 8 slag compositions were prepared. Out of them 4 are obtained by keeping the  $\text{MgO}$  content constant at 4% and varying the basicity of the slag from 0.9 to 1.2. While the rest of the 4 are obtained by keeping the basicity constant at 0.9 and varying the  $\text{MgO}$  content from 4% to 10%. The hemispherical temperatures (experimental results) of these slags ranged from 1291K to 1404K. Based on these liquidus temperatures the range of temperature for calculation of viscosity is selected to be 1250K to 1450K.

**Table 2:** Values to calculate Iida model.

<b>Component</b>	<b><math>T_m</math> (inK)</b>	<b><math>\rho_m</math> (<math>10^3\text{kg/m}^3</math>)</b>	<b><math>M_i</math> (<math>10^3\text{kg/mol}</math>)</b>	<b><math>(V_m)_i</math> (<math>10^{-6}\text{m}^3/\text{mol}</math>)</b>	<b><math>\mu_{oi}</math> (mPas)</b>	<b><math>\alpha_i</math></b>
$\text{SiO}_2$	2001	2.2	60.08	27.29	$0.1317 \exp(5613.5/T)$	1.48
$\text{Al}_2\text{O}_3$	2313	3.04	101.96	33.58	$0.14792 \exp(6679.5/T)$	0.1
$\text{CaO}$	2873	2.39	56.08	23.49	$0.13651 \exp(8664.4/T)$	1.53
$\text{MgO}$	3073	2.49	40.3	16.16	$0.1474 \exp(9393.1/T)$	1.51

**Table 3:** Composition of various slag samples along with their liquidus temperatures.

<b>Sample</b>	<b>C/S</b>	<b><math>W_{\text{MgO}}</math> %</b>	<b><math>W_{\text{Al}_2\text{O}_3}</math> %</b>	<b><math>W_{\text{CaO}}</math> %</b>	<b><math>W_{\text{SiO}_2}</math> %</b>	<b>HT</b>
Slag 1	0.9	4	25	33.63	37.37	1291
Slag 2	1	4	25	35.5	35.5	1329
Slag 3	1.1	4	25	37.19	33.81	1366
Slag 4	1.2	4	25	38.73	32.27	1404
Slag 5	0.9	4	25	33.63	37.37	1291
Slag 6	0.9	6	25	32.68	36.32	1296
Slag 7	0.9	8	25	31.74	35.26	1301
Slag 8	0.9	10	25	30.79	34.21	1307

Table 4: Amount of oxides required to prepare slags.

Sample	$W_{\text{MgO}}$ %	$W_{\text{Al}_2\text{O}_3}$ %	$W_{\text{CaO}}$ %	$W_{\text{SiO}_2}$ %	MgO (gms)	$\text{Al}_2\text{O}_3$ (gms)	CaO (gms)	$\text{SiO}_2$ (gms)
Slag 1	4	25	33.63	37.37	4.8	30	40.356	44.844
Slag 2	4	25	35.5	35.5	4.8	30	42.6	42.6
Slag 3	4	25	37.19	33.81	4.8	30	44.628	40.572
Slag 4	4	25	38.73	32.27	4.8	30	46.476	38.724
Slag 5	4	25	33.63	37.37	4.8	30	40.356	44.844
Slag 6	6	25	32.68	36.32	7.2	30	39.216	43.584
Slag 7	8	25	31.74	35.26	9.6	30	38.088	42.312
Slag 8	10	25	30.79	34.21	12	30	36.948	41.052

Table 5: Mole fractions of components of the slag.

Sample	$X_{\text{MgO}}$	$X_{\text{Al}_2\text{O}_3}$	$X_{\text{CaO}}$	$X_{\text{SiO}_2}$
Slag 1	0.063376	0.15656	0.382904	0.397159
Slag 2	0.063287	0.156339	0.403624	0.376751
Slag 3	0.063206	0.156139	0.422298	0.358357
Slag 4	0.063132	0.155957	0.439274	0.341637
Slag 5	0.063376	0.15656	0.382904	0.397159
Slag 6	0.09415	0.155054	0.368509	0.382287
Slag 7	0.124336	0.153576	0.354496	0.367591
Slag 8	0.153954	0.152127	0.340641	0.353279

By experimental data we obtained the values of a b & c for the calculation of  $\alpha^*_{Al_2O_3}$  as follows [18]:

$$a = -4.43 \times 10^{-6} T^2 + 1.4 \times 10^{-2} T - 10.06$$

$$b = 2.57 \times 10^{-7} T^2 - 6.38 \times 10^{-4} T + 0.368$$

$$c = -6.86 \times 10^{-6} T^2 + 1.7 \times 10^{-2} T - 10.77$$

here T is in °C.

Table 6: Values of a b & c.

Temp (°C)	a	b	c
1250	0.518125	-0.0279375	-0.23875
1300	0.6533	-0.02707	-0.2634
1350	0.766325	-0.0249175	-0.32235
1400	0.8572	-0.02148	-0.4156
1450	0.925925	-0.0167575	-0.54315

#### **4.1 CALCULATIONS:**

- First we need to calculate  $\mu_{O_i}$  for every oxide.
- Suppose for Slag 1 whose  $X_i$  values are shown in table 5 we calculate  $\mu_{O_i}$  by using formula given in table 2 for each oxide. This short formula is obtained by substituting values shown in table 2 in equation 4. After that we will calculate  $\mu_o$  value by equation 4.2. Now we calculate  $B_i^{(i)}$  with the help of  $\alpha^*_{Al_2O_3}$  & a, b, c values given in table 6. A & E are calculated as per there equations given in modified Iida model at a fixed absolute temperature.  $\mu_o$  for slag 1 will be 45.575 m Pas so by using these values we can easily get  $\mu$  value.

Table 7: Values of A & E at different temperatures.

Temp (K)	A	E
1523	0.299711	5.931784
1573	0.358351	5.506784
1623	0.422241	5.101784
1673	0.491381	4.716784

Table 8: Calculated Viscosities of different slag composition at 1523 K.

Sample	$B_i$	$\alpha_{Al_2O_3}^*$	$B_i^{(j)}$	$\mu_o$ (mPas)	$\mu$ (Pas)
Slag 1	0.994573	-0.421937	1.284516	45.57330812	1.3833647
Slag 2	1.096566	-0.369092	1.393471	44.97115422	0.95136738
Slag 3	1.197985	-0.316544	1.494134	44.42842628	0.70554092
Slag 4	1.299193	-0.264106	1.586534	43.93507571	0.55367735
Slag 5	0.994573	-0.421937	1.284516	45.57330812	1.3833647
Slag 6	1.049895	-0.393273	1.344672	44.09027944	1.0885489
Slag 7	1.108941	-0.36268	1.406431	42.63236823	0.86719771
Slag 8	1.170859	-0.330598	1.468369	41.20509724	0.70156105

Table 9: Calculated Viscosities of different slag composition at 1573 K.

Sample	$B_i$	$\alpha_{Al_2O_3}^*$	$B_i^{(j)}$	$\mu_o$ (mPas)	$\mu$ (Pas)
Slag 1	0.994573	-0.421937	1.284516	37.76638479	0.98459056
Slag 2	1.096566	-0.369092	1.393471	37.28180214	0.69513777
Slag 3	1.197985	-0.316544	1.494134	36.84504247	0.5264103
Slag 4	1.299193	-0.264106	1.586534	36.44801917	0.42014402
Slag 5	0.994573	-0.421937	1.284516	37.76638479	0.98459056
Slag 6	1.049895	-0.393273	1.344672	36.55009855	0.78658623
Slag 7	1.108941	-0.36268	1.406431	35.35446076	0.63562834
Slag 8	1.170859	-0.330598	1.468369	34.18390298	0.52101779

Table 10: Calculated Viscosities of different slag composition at 1623 K.

Sample	$B_i$	$\alpha_{Al_2O_3}^*$	$B_i^{(j)}$	$\mu_o$ (mPas)	$\mu$ (Pas)
Slag 1	0.994573	-0.421937	1.284516	31.66694678	0.70970502
Slag 2	1.096566	-0.369092	1.393471	31.27200415	0.51375686
Slag 3	1.197985	-0.316544	1.494134	30.91603801	0.39688169
Slag 4	1.299193	-0.264106	1.586534	30.59245766	0.32190413
Slag 5	0.994573	-0.421937	1.284516	31.66694678	0.70970502
Slag 6	1.049895	-0.393273	1.344672	30.65772235	0.57523447
Slag 7	1.108941	-0.36268	1.406431	29.66566867	0.47119886
Slag 8	1.170859	-0.330598	1.468369	28.69438749	0.39110576

Table 11: Calculated Viscosities of different slag composition at 1673 K.

Sample	$B_i$	$\alpha_{Al_2O_3}^*$	$B_i^{(j)}$	$\mu_o$ (mPas)	$\mu$ (Pas)
Slag 1	0.994573	-0.421937	1.284516	26.83803997	0.51869502
Slag 2	1.096566	-0.369092	1.393471	26.51241027	0.38451963
Slag 3	1.197985	-0.316544	1.494134	26.21891664	0.30272159
Slag 4	1.299193	-0.264106	1.586534	25.95212505	0.24931819
Slag 5	0.994573	-0.421937	1.284516	26.83803997	0.51869502
Slag 6	1.049895	-0.393273	1.344672	25.9916863	0.42623819
Slag 7	1.108941	-0.36268	1.406431	25.15976163	0.35369562
Slag 8	1.170859	-0.330598	1.468369	24.34522757	0.29709746



Table 12: Calculated Viscosities of different slag composition at 1723 K.

Sample	$B_i$	$\alpha_{Al_2O_3}^*$	$B_i^{(j)}$	$\mu_o$ (mPas)	$\mu$ (Pas)
Slag 1	0.994573	-0.421937	1.284516	22.96841691	0.3846877
Slag 2	1.096566	-0.369092	1.393471	22.69707858	0.29167842
Slag 3	1.197985	-0.316544	1.494134	22.45251836	0.23378833
Slag 4	1.299193	-0.264106	1.586534	22.23020822	0.1953586
Slag 5	0.994573	-0.421937	1.284516	22.96841691	0.3846877
Slag 6	1.049895	-0.393273	1.344672	22.25173294	0.32027164
Slag 7	1.108941	-0.36268	1.406431	21.54729042	0.26904758
Slag 8	1.170859	-0.330598	1.468369	20.85755076	0.22856828

#### 4.2 Effect of basicity on viscosity:

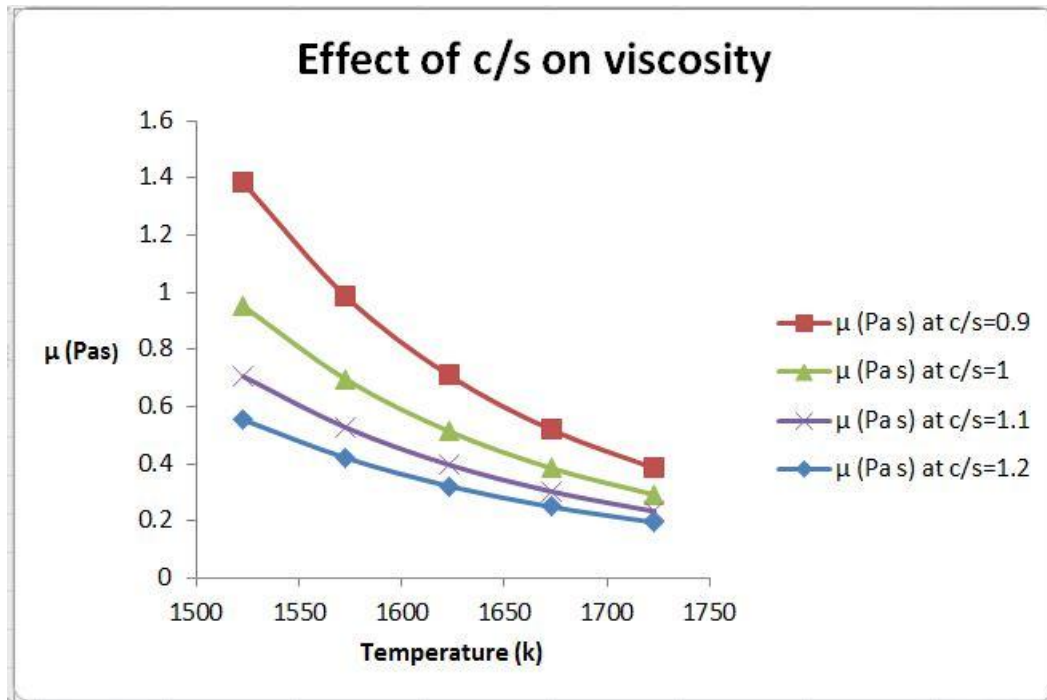


Fig.3: Effect of temperature on viscosity at different C/S ratios.

We can see from the graph that with increase in temperature viscosity will decrease as expected. Now with increasing c/s ratio viscosity is decreasing. This happens because of depolymerization taking place at high CaO contents. CaO will break  $SiO_2$  network & combine with  $Al^{+3}$  ions

present in this network. The excess  $\text{Ca}^{+2}$  ions will break the already existing aluminosilicate network. This breaking of network results in low viscosity at high C/S ratios. We can see from Table 3 that with increasing C/S ratio HT also increases. So basicity affects viscosity in two ways.

#### **4.3 Effect of MgO content on viscosity:**

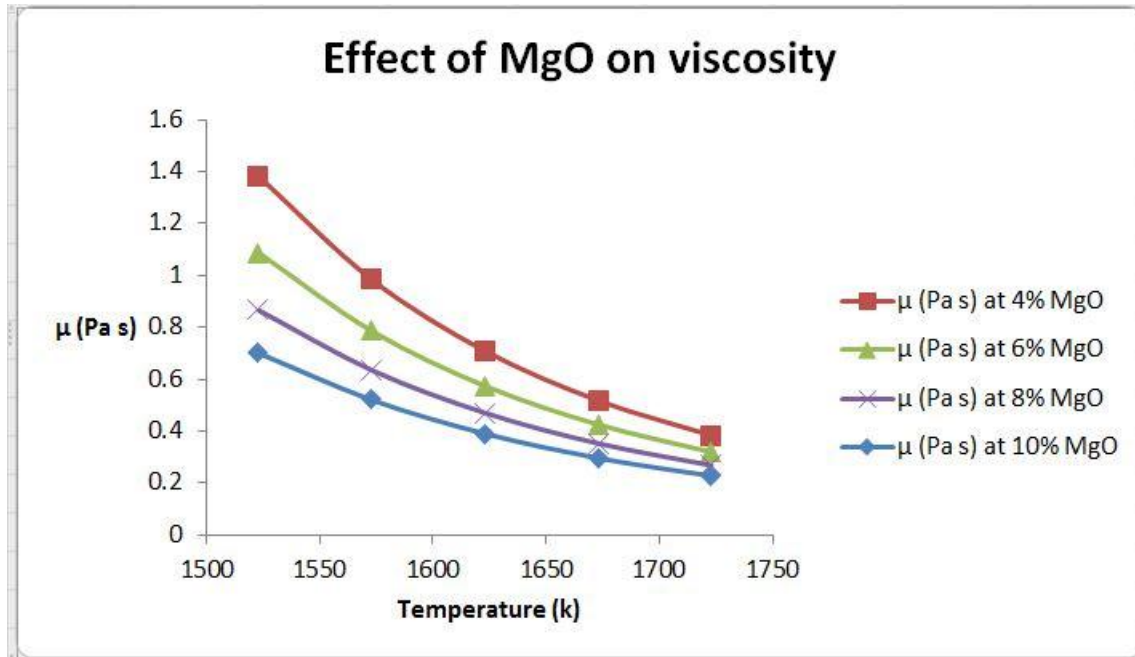


Fig.4: Effect of temperature on viscosity at different MgO concentrations.

Similar to basicity, with increasing MgO, the viscosity will decrease at constant C/S & alumina content. MgO has a similar role as basicity. It also affects viscosity in two ways. We can see from Table 3 that HT increases with increasing MgO. MgO plays a role of network modifier in slag, same as that of CaO & other basic oxides. CaO is stronger than MgO so at high basicity, the effect of MgO is very less in controlling viscosity of slag. The capacity of any basic oxide in decreasing viscosity is based upon its basicity of oxides, i.e. tendency to give its  $\text{O}^{2-}$  ion.  $\text{MgO}$   $Z/r^2$  ( $Z$  atomic number &  $r$  = radius) is much higher than CaO. So polarizing power of MgO is more than CaO. Thus MgO will hold on to its  $\text{O}^{2-}$  ion more rigidly than CaO. Thus CaO is a stronger network breaker than MgO. Both of these oxides will basically break the complex slag network into a simpler slag network thus decreasing the viscosity.

#### **4.4 Effect of temperature on viscosity:**

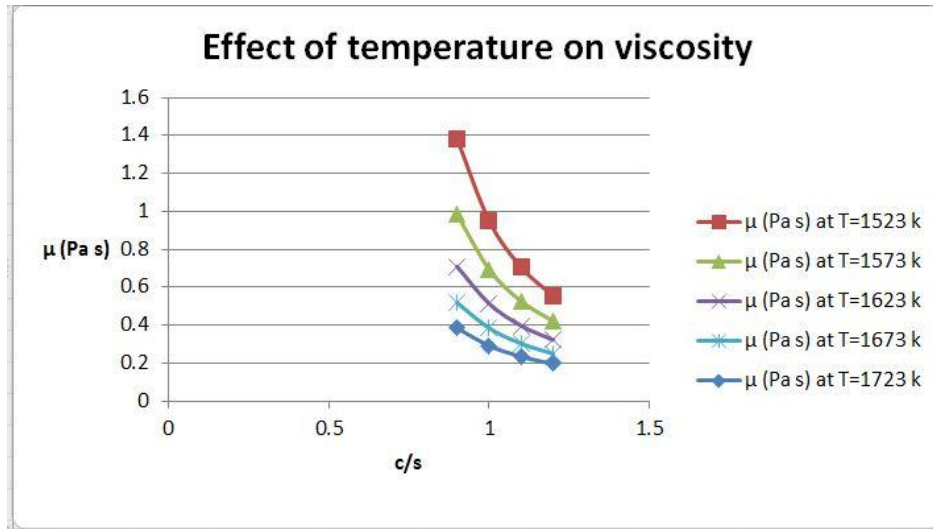


Fig.5: Effect of basicity on viscosity at different temperature.

At higher temperature C/S ratio's effect on viscosity is less pronounced as compared to that at low temperature. This is because many of the complex network will already break into simpler network due to thermal energies at such high temperature so only few networks will be left to deal with for CaO & thus less effect will be there. We can see this from the graph.

#### **4.5 Effect of viscosity by varying basicity and temperature:**

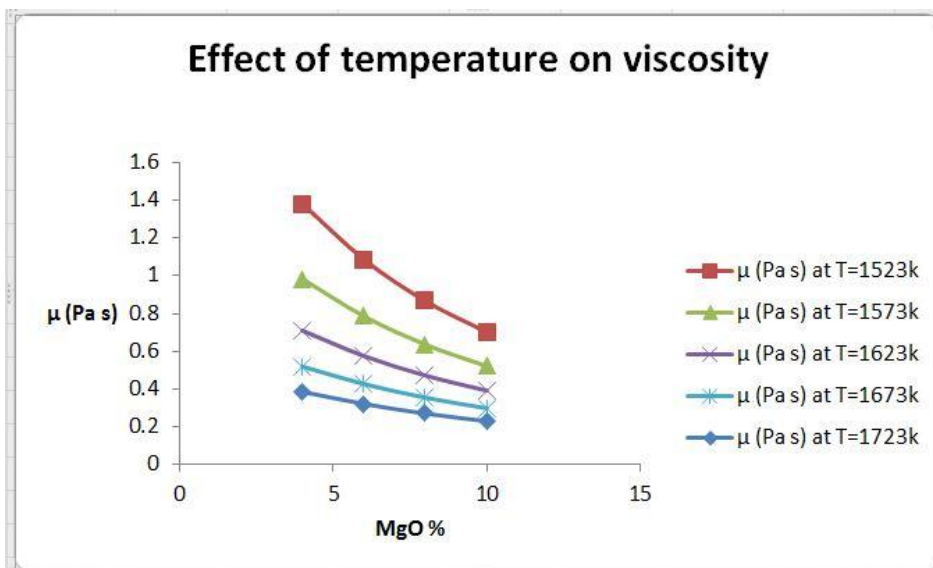


Fig.6: Effect of MgO on viscosity at different temperature.

Similar to C/S ratio, at high temperature increasing MgO will not produce pronounced effect on viscosity of slag.

## **5. CONCLUSION:**

We calculated the viscosity of high alumina slag at different MgO & C/S ratios. Based on the statistical calculations done with the help of iida model, following conclusions can be made:

1. With the increasing temperature, the viscosity of any composition of slag decreases.
2. With the increasing MgO content, viscosity decreases at constant C/S ratio & Al<sub>2</sub>O<sub>3</sub> composition.
3. MgO's effect is not pronounced at high temperature which is similar to that of effect of C/S ratio.
4. With the increasing C/S ratio, the viscosity decreases (at constant MgO & Al<sub>2</sub>O<sub>3</sub> composition) & this effect is more pronounced than MgO.
5. Low viscosity will be obtained when slag has higher MgO, higher basicity conditions.

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